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DESCRIPTION

HYDROGEN ABSORBING ALLOY FOR ALKALINE STORAGE BATTERY
AND METHOD OF PRODUCING THE SAME, AND HYDROGEN ABSORBING
ALLOY ELECTRODE FOR ALKALINE STORAGE BATTERY AND METHOD OF
PRODUCING THE SAME

Technical Field

The present invention relates generally to a hydrogen absorbing alloy for an alkaline storage battery used as a negative electrode material for an alkaline storage battery and a method of producing the same, and a hydrogen absorbing alloy electrode for an alkaline storage battery and a method of producing the same, and is particularly characterized in that the hydrogen absorbing alloy is treated to enhance the activity in the early stages of the hydrogen absorbing alloy, to increase an initial discharge capacity as well as to improve high-rate discharge characteristics in the alkaline storage battery using the hydrogen absorbing alloy.

Background Art

Conventionally, nickel-cadmium storage batteries have been generally used as alkaline storage batteries. However, in recent years, nickel-hydrogen storage batteries

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cannot be greatly improved.

Disclosure of Invention

The present invention solves various problems, as described above, in an alkaline storage battery using a hydrogen absorbing alloy as a negative electrode material.

Specifically, an object of the present invention is to enhance the activity in the early stages of a hydrogen absorbing alloy used as a negative electrode material of an alkaline storage battery, to increase an initial battery capacity and improve high-rate discharge characteristics in the alkaline storage battery using the hydrogen absorbing alloy.

A hydrogen absorbing alloy for an alkaline storage battery in the present invention is a hydrogen absorbing alloy having a crystal structure of a CaCu_5 type and represented by a composition formula $\text{MmNi}_x\text{Co}_y\text{Mn}_z\text{M}_{1-z}$ (in the formula, M is at least one element selected from aluminum Al and copper Cu, x is a composition ratio of nickel Ni and satisfies $3.0 \leq x \leq 5.2$, y is a composition ratio of cobalt Co and satisfies $0 \leq y \leq 1.2$, and z is a composition ratio of manganese Mn and satisfies $0.1 \leq z \leq 0.9$, with the proviso that the sum of x, y, and z satisfies $4.4 \leq x + y + z \leq 5.4$), which has a surface region and a bulk region covered with the surface region, the surface

region and the bulk region differing in composition, and satisfies the condition of $a/b \geq 1.2$, letting a be the sum of the respective abundance ratios of atoms Ni, Co, and Mn in the surface region and letting b the sum of the respective abundance ratios of atoms Ni, Co, and Mn.

The surface region and the bulk region in the hydrogen absorbing alloy are definitely distinguished by observation using a scanning type transmission electron microscope (TEM), and differ in composition. The surface region is normally formed to a depth of approximately 80 nm from the surface of the hydrogen absorbing alloy.

In determining the surface region and the bulk region in the present invention, analysis is performed using the scanning type transmission electron microscope and an energy dispersion type X-ray analysis meter at spacing of several nanometers from the surface of each of the particles of the hydrogen absorbing alloy toward the center thereof, and the respective abundance ratios of metal elements at each of points of measurement are found. The respective abundance ratios of the metal elements are constant in a region inside of a certain point of measurement. The point of measurement is taken as the boundary, to take a region on the side of the surface from the point of measurement as the surface region and take a region on the side of the center from the point of

measurement as the bulk region.

The sum a of the respective abundance ratios (atm%) of the atoms Ni, Co, and Mn in the surface region is a value measured at a middle point between the surface of each of the particles of the hydrogen absorbing alloy and the boundary, and the sum b of the respective abundance ratios (atm%) of the atoms Ni, Co, Mn in the bulk region is a value measured at a point on the side of the center of each of the particles of the hydrogen absorbing alloy from the boundary in which the respective abundance ratios of the metal elements are constant, as described above.

When a hydrogen absorbing alloy having a crystal structure of a CaCu_5 type and represented by a composition formula $\text{MmNi}_x\text{Co}_y\text{Mn}_z\text{M}_{1-z}$ (in the formula, M is at least one element selected from aluminum Al and copper Cu, x is a composition ratio of nickel Ni and satisfies $3.0 \leq x \leq 5.2$, y is a composition ratio of cobalt Co and satisfies $0 \leq y \leq 1.2$, and z is a composition ratio of manganese Mn and satisfies $0.1 \leq z \leq 0.9$, with the proviso that the sum of x, y, and z satisfies $4.4 \leq x + y + z \leq 5.4$) is used as a negative electrode material of an alkaline storage battery, as in the hydrogen absorbing alloy for an alkaline storage battery in the present invention, the hydrogen absorbing alloy is prevented from being corroded in an alkaline electrolyte, to prevent the amount of

appear on the surface of the particle of the hydrogen absorbing alloy.

In the second step, examples of the acid solution for treating the particles of the hydrogen absorbing alloy include hydrochloric acid, sulfuric acid, and phosphoric acid.

In treating the particles of the hydrogen absorbing alloy in such an acid solution, when the pH of the acid solution is too low, the particles of the hydrogen absorbing alloy are rapidly oxidized, so that nickel and cobalt on the surface of each of the particles of the hydrogen absorbing alloy are also dissolved. On the other hand, when the pH of the acid solution is high, the oxide coating on the surface of the particle of the hydrogen absorbing alloy is not sufficiently removed. Therefore, it is preferable that the pH in the early stages of the acid solution is in the range of 0.7 to 2.0.

In thus treating the particles of the hydrogen absorbing alloy in the acid solution, it is preferable that a nickel compound and a cobalt compound are added to the acid solution. Examples of the nickel compound to be added to the acid solution include nickel chloride NiCl_2 and nickel hydroxide $\text{Ni}(\text{OH})_2$. Examples of the cobalt compound include cobalt chloride CoCl_2 and cobalt hydroxide $\text{Co}(\text{OH})_2$.

When the nickel compound and the cobalt compound are

thus added to the acid solution to treat the particles of the hydrogen absorbing alloy, the nickel compound and the cobalt compound which have been added to the acid solution are respectively reduced to metal nickel and metal cobalt. The metal nickel and the metal cobalt thus reduced are deposited on the surface of the hydrogen absorbing alloy, so that a lot of active metal nickel and metal cobalt appear on the surface of each of the particles of the hydrogen absorbing alloy.

When the respective amounts of the nickel compound and the cobalt compound to be added to the acid solution are small, the respective amount of the metal nickel and the metal cobalt to be deposited on the surface of the hydrogen absorbing alloy are reduced, so that a lot of active metal nickel and metal cobalt cannot appear on the surface of each of the particles of the hydrogen absorbing alloy. On the other hand, when the respective amounts of the nickel compound and the cobalt compound to be added are too large, the respective amounts of the metal nickel and metal cobalt to be deposited on the surface of the particle of the hydrogen absorbing alloy are excessive.

Accordingly, the surface of the particle of the hydrogen absorbing alloy is easily oxidized. Therefore, it is preferable that the respective amounts of the nickel compound and the cobalt compound to be added to the acid

alloy electrode using the particles of the hydrogen absorbing alloy is used as the alkaline storage battery, the manganese or an oxide of the manganese on the surface of the particle of the hydrogen absorbing alloy is gradually dissolved in the alkaline electrolyte in the alkaline storage battery, not to degrade the activity on the surface of the particle of the hydrogen absorbing alloy.

When the particles of the hydrogen absorbing alloy are treated in the acid solution in the second step, and the particles of the hydrogen absorbing alloy are then heat-treated and sintered at a temperature of not more than the melting point of the particles of the hydrogen absorbing alloy in the hydrogen atmosphere in the third step, as described above, a surface region 1b where the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms are higher than those in an inner bulk region 1a is formed, and the particles 1 of the hydrogen absorbing alloy are welded together in the surface region 1b. Accordingly, contact resistance between the particles 1 of the hydrogen absorbing alloy is reduced.

A conductive core member is filled with the particles of the hydrogen absorbing alloy thus obtained, to produce a hydrogen absorbing alloy electrode for an alkaline storage battery.

battery in each of examples of the present invention and a method of producing the same as well as a hydrogen absorbing alloy electrode for an alkaline storage battery and a method of producing the same will be specifically described, and a comparative example is taken, to clarify that those in the examples of the present invention are superior. The hydrogen absorbing alloy for an alkaline storage battery in the present invention and the method of producing the same as well as the hydrogen absorbing alloy electrode for an alkaline storage battery and the method of producing the same are not limited to those in the following examples, and can be embodied by being suitably changed in a range in which the gist thereof is not changed.

(Examples 1 to 10)

In the examples, in producing particles of a hydrogen absorbing alloy, as shown in the foregoing first step, Misch metal (Mm) which is a mixture of rare earth elements containing 25 % by weight of La, 50 % by weight of Ce, 7 % by weight of Pr, and 18 % by weight of Nd and Ni, Co, Mn and Al having a purity of 99.9 % were mixed at a molar ratio of 1.0 : 3.1 : 0.9 : 0.6 : 0.4. A mixture obtained was dissolved by an arc melting furnace in an argon atmosphere, and was then naturally cooled, to produce an ingot of a hydrogen absorbing alloy indicated by a

composition formula $MmNi_{3.1}Co_{0.9}Mn_{0.6}Al_{0.4}$. The ingot of the hydrogen absorbing alloy was mechanically ground in the air and classified, to obtain particles of the hydrogen absorbing alloy having an average particle diameter of 80 μm .

In then treating the particles of the hydrogen absorbing alloy in an acid solution, as shown in the foregoing second step, a hydrochloric acid solution was used as the acid solution. Nickel chloride $NiCl_2$, which is a nickel compound was contained in the hydrochloric acid solution at a ratio of 0 % by weight to 10.0 % by weight, as shown in the following Table 1, to the particles of the hydrogen absorbing alloy, and the pH of the hydrochloric acid solution was adjusted to 1.0. The particles of the hydrogen absorbing alloy were treated upon being immersed in the hydrochloric acid solution for thirty minutes while being agitated. Thereafter, the particles of the hydrogen absorbing alloy thus treated were sucked in and filtered, and were rinsed and dried.

In heat-treating and sintering the particles of the hydrogen absorbing alloy thus treated in the acid solution at a temperature of not more than the melting point under a hydrogen atmosphere, as shown in the foregoing third step, the particles of the hydrogen absorbing alloy were sintered at a temperature of 600°C under the hydrogen atmosphere for

six hours, to obtain particles of each of the hydrogen absorbing alloys in the examples 1 to 10. The melting point of the particles of the hydrogen absorbing alloy was approximately 1200°C.

(Comparative Example 1)

In the comparative example 1, particles of a hydrogen absorbing alloy indicated by a composition formula $\text{MmNi}_{3.1}\text{Co}_{0.9}\text{Mn}_{0.6}\text{Al}_{0.4}$ produced in the same manner as that in the first step in each of the examples 1 to 10 were used.

In treating the particles of the hydrogen absorbing alloy in an acid solution, nickel chloride NiCl_2 , which is a nickel compound was not added to a hydrochloric acid solution, and the particles of the hydrogen absorbing alloy were immersed in the hydrochloric acid solution having a pH of 0.3 and having a liquid temperature of 25°C for thirty minutes while being agitated. Thereafter, the particles of the hydrogen absorbing alloy thus treated were sucked in and filtered, and were rinsed and dried.

The particles of the hydrogen absorbing alloy thus treated were then sintered at a temperature of 600°C under a hydrogen atmosphere for six hours, as in the examples 1 to 10, to obtain particles of the hydrogen absorbing alloy in the comparative example 1.

With respect to the particles of each of the hydrogen absorbing alloys in the examples 1 to 10 and the

comparative example 1 obtained in the above-mentioned manner, the abundance ratio (atm%) of each of atoms in a surface region and the abundance ratio (atm%) of the atom in an inner bulk region were respectively measured using a scanning type transmission electron microscope and an energy dispersion type X-ray analysis meter.

With respect to the particles of each of the hydrogen absorbing alloys in the examples 1 to 10 and the comparative example 1, the sum a (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms in the surface region and the sum b (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms in the bulk region were found, to calculate the value of a/b. The results thereof were together shown in the following Table 1. In the particles of the hydrogen absorbing alloy in the example 1, in the surface region, the abundance ratio of the nickel atoms was 70.7 atm%, the abundance ratio of the cobalt atoms was 16.7 atm%, the abundance ratio of the manganese atoms was 4.6 atm%, and the sum a of the abundance ratios was 92.0 atm%. On the other hand, in the bulk region, the abundance ratio of the nickel atoms was 51.7 atm%, the abundance ratio of the cobalt atoms was 15.1 atm%, the abundance ratio of the manganese atoms was 9.9 atm%, and the sum b of the abundance ratios was 76.7 atm%. The value of a/b was 1.20.

were together shown in the following Table 1.

In finding the initial discharge capacity, each of the alkaline storage batteries produced in the above-mentioned manner was charged at a current value of 0.2 C under room temperature for six hours, and was then discharged to 1.0 V at a current value of 0.2 C, to measure a discharge capacity in the first cycle. The discharge capacity in the first cycle was taken as an initial discharge capacity.

In finding the high-rate discharge capacity, the initial discharge capacity was found in the above-mentioned manner, and each of the alkaline storage batteries was then charged and discharged in three cycles in the same manner as described above. Thereafter, the alkaline storage battery was charged at a current value of 0.2 C under room temperature for six hours, and was discharged to 1.0 V at a high current value of 6.0 C. The discharge capacity was measured, and was taken as a high-rate discharge capacity.

(Table 1).

	acid solution		a/b	initial discharge capacity (mAh)	high-rate discharge capacity (mAh)
	pH	content of NiCl_2			
example 1	1.0	no added	1.20	730	730
example 2	1.0	0.3 % by weight	1.21	810	800
example 3	1.0	0.5 % by weight	1.22	820	815
example 4	1.0	0.7 % by weight	1.23	830	830
example 5	1.0	1.0 % by weight	1.24	830	835
example 6	1.0	2.0 % by weight	1.26	840	835
example 7	1.0	3.0 % by weight	1.27	840	840
example 8	1.0	5.0 % by weight	1.28	820	835
example 9	1.0	7.0 % by weight	1.29	780	775
example 10	1.0	10.0 % by weight	1.29	770	760
comparative example 1	0.3	no added	1.14	670	690

As a result, in the particles of each of the hydrogen absorbing alloys in the examples 1 to 10 so adapted that in the second step in which the particles of the hydrogen absorbing alloy were treated in the acid solution, the particles of the hydrogen absorbing alloy were treated in a hydrochloric acid solution containing 0 % by weight to

10.0 % by weight of nickel chloride NiCl_2 , which is a nickel compound in the particles of the hydrogen absorbing alloy and having a pH adjusted to 1.0, the ratio (a/b) of the sum a (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms in the surface region to the sum b (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms in the bulk region was not less than 1.20, and the value of a/b was increased as the amount of the nickel chloride NiCl_2 , contained in the hydrochloric acid solution was increased.

On the other hand, in the particles of the hydrogen absorbing alloy in the comparative example 1 in which in treating the particles of the hydrogen absorbing alloy in the acid solution, the particles of the hydrogen absorbing alloy were treated in a hydrochloric acid solution containing no nickel chloride NiCl_2 , which is a nickel compound and having a pH adjusted to 0.3, the inside of each of the particles of the hydrogen absorbing alloy was also dissolved by the hydrochloric acid solution, and the value of a/b was as low as 1.14.

In the alkaline storage battery produced using the particles of each of hydrogen absorbing alloys in the examples 1 to 10 in which the value of a/b was not less than 1.20, the initial discharge capacity and the high-rate

discharge capacity were made larger, as compared with those in the alkaline storage battery produced using the particles of the hydrogen absorbing alloy in the comparative example 1 in which the value of a/b was as low as 1.14. Particularly, in the alkaline storage battery using the particles of each of the hydrogen absorbing alloys in the examples 2 to 8 treated using a hydrochloric acid solution containing 0.3 % by weight to 5.0 % by weight of nickel chloride NiCl_2 to be contained in the hydrochloric acid solution to the particle of the hydrogen absorbing alloy, the initial discharge capacity assumed a high value of 800 mAh to 840 mAh, and the high-rate discharge capacity assumed a high value of 800 mAh to 840 mAh. In treating the particles of the hydrogen absorbing alloy in the hydrochloric acid solution, it was preferable that 0.3 % by weight to 5.0 % by weight of NiCl_2 was added to the particles of the hydrogen absorbing alloy.

Although in the examples 1 to 10, the hydrochloric acid solution was used as the acid solution in the second step, the same effect also appeared in a case where a nitric acid solution, a phosphoric acid solution, or the like was used. Further, nickel chloride NiCl_2 was contained in the hydrochloric acid solution. However, the same effect also appeared in a case where another nickel compound such as nickel hydroxide $\text{Ni}(\text{OH})_2$ or a cobalt

compound such as cobalt chloride CoCl_2 , or cobalt hydroxide $\text{Co}(\text{OH})_2$ was contained.

(Examples 11 to 15)

Also in the examples 11 to 15, particles of a hydrogen absorbing alloy represented by a composition formula $\text{MmNi}_{3.1}\text{Co}_{0.9}\text{Mn}_{0.6}\text{Al}_{0.4}$ produced in the same manner as that in the foregoing first step in each of the examples 1 to 10 were used.

In treating the particles of the hydrogen absorbing alloy in an acid solution, as shown in the foregoing second step, 0.3 % by weight of nickel chloride NiCl_2 which is a nickel compound was contained in the particles of the hydrogen absorbing alloy, as in the example 7, while the particles of the hydrogen absorbing alloy were treated in the hydrochloric acid solution in the same manner as those in the examples 1 to 10 except that the pH of the hydrochloric acid solution was changed in the range of 0.3 to 3.0, as shown in the following Table 2.

In heat-treating and sintering the particles of each of the hydrogen absorbing alloys thus treated in the acid solution at a temperature of not more than the melting point under a hydrogen atmosphere, as in the third step, the particles of the hydrogen absorbing alloy were sintered at a temperature of 600°C under a hydrogen atmosphere for six hours, as in the examples 1 to 10.

With respect to the particles of each of the hydrogen absorbing alloys in the examples 11 to 15 thus obtained, the sum a (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms in a surface region and the sum b (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms and manganese atoms in a bulk region were also found, as in the examples 1 to 10, to calculate the value of a/b. The results thereof were together shown in the following Table 2.

A hydrogen absorbing alloy electrode was produced, as in the examples 1 to 10, using the particles of each of the hydrogen absorbing alloys in the examples 11 to 15 obtained in the above-mentioned manner, and an alkaline storage battery of a positive electrode control type of AA size and having a battery capacity of 1000 mAh was produced using the hydrogen absorbing alloy.

With respect to each of the alkaline storage batteries, an initial discharge capacity (mAh) and a high-rate discharge capacity (mAh) were also found, as in the examples 1 to 10. The results thereof, together with those in the example 7, were shown in the following Table 2.

(Table 2)

	acid solution		a/b	initial discharge capacity (mAh)	high-rate discharge capacity (mAh)
	pH	content of NiCl_2			
example 11	0.3	3.0 % by weight	1.20	770	780
example 12	0.5	3.0 % by weight	1.22	790	795
example 13	0.7	3.0 % by weight	1.25	830	840
example 7	1.0	3.0 % by weight	1.27	840	840
example 14	2.0	3.0 % by weight	1.25	830	835
example 15	3.0	3.0 % by weight	1.20	790	795

As a result, in the particles of each of the hydrogen absorbing alloys in the examples 7 and 11 to 15 so adapted that in the second step in which the particles of the hydrogen absorbing alloy were treated in the acid solution, the particles of the hydrogen absorbing alloy were treated in a hydrochloric acid solution containing 3.0 % by weight of nickel chloride NiCl_2 , which is a nickel compound in the particles of the hydrogen absorbing alloy and having a pH adjusted in the range of 0.3 to 3.0, the ratio (a/b) of the sum a (atm%) of the respective abundance ratios of nickel atoms, cobalt atoms, and manganese atoms in the surface region to the sum b (atm%) of the respective abundance

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ratios of nickel atoms, cobalt atoms, and manganese atoms in the bulk region was not less than 1.20. Particularly in the particles of the hydrogen absorbing alloy in the example 7 treated using a hydrochloric acid solution having a pH of 1.0, the value of a/b was the highest, i.e., 1.27. The reason for this is conceivably that the nickel atoms and the cobalt atoms in the surface region were also dissolved, and the respective numbers of the nickel atoms and the cobalt atoms in the surface region were reduced when the pH of the hydrochloric acid solution is too low, while an oxide coating on the surface of each of the particles of the hydrogen absorbing alloy was not sufficiently removed when the pH of the hydrochloric acid solution was increased.

Also in the alkaline storage battery produced using the particles of each of the hydrogen absorbing alloys in the examples 11 to 15, the initial discharge capacity and the high-rate discharge capacity were larger, as compared with those in the alkaline storage battery produced using the particles of the hydrogen absorbing alloy in the comparative example 1. Particularly in the alkaline storage battery using the particles of each of the hydrogen absorbing alloys in the examples 13, 7, and 14 treated with the pH of the hydrochloric acid solution set in the range of 0.7 to 2.0, the initial discharge capacity assumed a

high value of 830 mAh to 840 mAh, and the high-rate discharge capacity assumed a high value of 835 mAh to 840 mAh. In treating the particles of the hydrogen absorbing alloy in the hydrochloric acid solution, it was preferable that the pH thereof was set in the range of 0.7 to 2.0.

Although in each of the examples 11 to 15, the hydrochloric acid solution was also used as the acid solution in the second step, the same effect also appeared in a case where a nitric acid solution, a phosphoric acid solution, or the like was used. Further, nickel chloride NiCl_2 was contained in the hydrochloric acid solution. However, the same effect also appeared in a case where another nickel compound such as nickel hydroxide $\text{Ni}(\text{OH})_2$ and a cobalt compound such as cobalt chloride CoCl_2 or cobalt hydroxide $\text{Co}(\text{OH})_2$ were contained.

Although in each of the examples, in producing the particles of the hydrogen absorbing alloy in the first step, the particles of the hydrogen absorbing alloy obtained by grinding the mass of the hydrogen absorbing alloy were produced using an arc furnace in an argon atmosphere, the particles of the hydrogen absorbing alloy can be also produced using a gas atomizing method or a roll quenching method. The same effect also appeared in a case where the particles of the hydrogen absorbing alloy, which were easy to sinter, thus obtained by the gas atomizing

method or the roll quenching method were used.

Industrial Applicability

As described in detail above, in a hydrogen absorbing alloy for an alkaline storage battery in the present invention and a hydrogen absorbing alloy for an alkaline storage battery obtained by a method of producing the hydrogen absorbing alloy for an alkaline storage battery in the present invention, a lot of active metal nickel and metal cobalt appear on the surface of each of particles of the hydrogen absorbing alloy, and the metal nickel and metal cobalt are prevented from being oxidized again. Further, the particles of the hydrogen absorbing alloy are welded together in a surface region in the hydrogen absorbing alloy.

When a hydrogen absorbing alloy electrode for an alkaline storage battery using the hydrogen absorbing alloy is used as a negative electrode of the alkaline storage battery, the activity in the early stages of the hydrogen absorbing alloy is enhanced, so that an initial battery capacity in the alkaline storage battery is improved. Further, contact resistance between the particles of the hydrogen absorbing alloy is reduced, so that high-rate discharge characteristics in the alkaline storage battery are also improved.